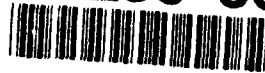


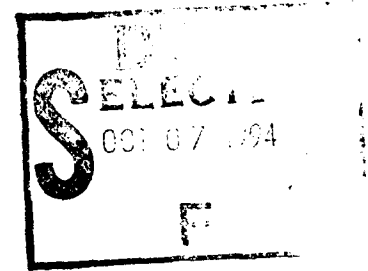
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**LIQUID XENON  
AS A  
POTENTIAL  
LASER HOST MEDIUM.**



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DISCONTINUED

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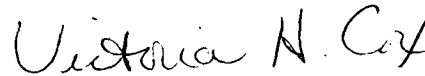
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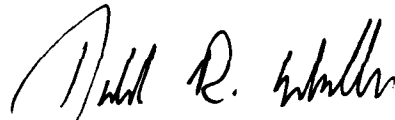
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This report has been reviewed and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.



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13. ABSTRACT (Maximum 200 words) This report describes preliminary attempts to investigate the feasibility of using liquid xenon as a solvent for novel laser systems. The objective was to see if the wide transparency range and low non radiative relaxation rates of this solvent can be exploited. A novel cell and filling system was successfully constructed. Barium fluoride windows repeatedly failed at a small fraction of their design pressure. They were successfully replaced with sapphire windows, but this severely limited the use of infrared diagnostics. As supplied xenon was found to be contaminated with excessive hydrocarbons (mainly methane) further limiting infrared diagnostics and nullifying the low non-radiative rate advantage of the solvent. Attempts to dissolve Rhodamine 6g and B were unsuccessful; there was limited evidence of p-terphenyl solubility. Overall the program was very seriously restricted by the combined problems of window failure and xenon contamination and the key concepts remain unproven, although methods to overcome these difficulties are identified.				
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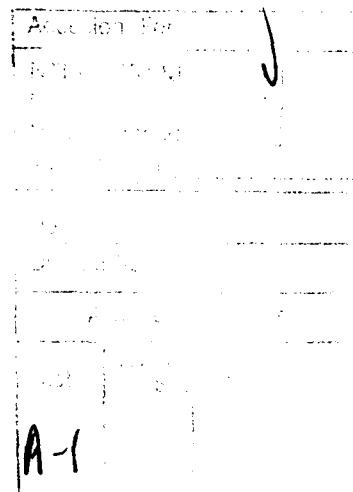
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## 1 Introduction and objectives.

Despite the long standing and intensive research in the laser field there remain extensive gaps in the availability of lasers for particular applications. A good example is the very small number of lasers in the important three to five micron atmospheric transmission band, where only the technologically inconvenient DF laser and the cryogenically cooled CO laser are well developed. In fact throughout the infrared from approximately three microns to longer wavelengths only gas lasers are available with significant power output powers; they are typically bulky and fragile. At shorter wavelengths solid state and, to a limited extent liquid phase (dye lasers) lasers dominate, with occasional exceptions such as the widely used (but bulky and inefficient) argon laser.

The objective of the research effort was to construct a xenon filling system and suitable cooled high pressure optical cells, and to conduct a *preliminary* investigation of the highly novel suggestion that liquid xenon might be used as a solvent for liquid phase lasers in the infrared and other spectral regions. Construction of operational lasers was specifically excluded. We provide in the next section an explanation of the rationale for this suggestion, in slightly modified form from that in the original proposal reflecting changes that have occurred in the concept as it has received further study.

### 1.1 Rationale

Most condensed phase lasers require the lasing species to be highly diluted in a suitable host to prevent concentration quenching effects and provide the required spectroscopic properties. Examples would be  $\text{Nd}^{3+}$  in YAG, glass, etc, typically with a concentration of  $\text{Nd}^{3+}$  in the low percent region. There are rare exceptions where an 'undiluted' material can be used, but in these the crystal lattice happens to provide adequate 'isolation' between adjacent ions.

Solid laser systems are in many ways the preferred host, owing their convenience. However development of a new laser crystal, and to a lesser extent even a glass, is a major undertaking. The great majority of available laser hosts are oxide based, limiting infrared transparency to at best five, and more often closer to three microns. In practice in oxide hosts laser action is difficult much beyond two microns owing to excessive non radiative relaxation rates. Fluoride hosts - unfortunately of limited availability, and mechanically very weak - extend transparency to typically eight microns and reduced non radiative rates extend laser

action to about three microns. In both oxides and fluorides there are exceptional, longer wavelength transitions, but they are rare.

As a rough 'rule of thumb' materials become opaque in bulk thicknesses (several millimetres to a few centimetres, typical of laser active media) when the infrared wavenumber is approximately three times the highest frequency infrared active phonon energy. Non radiative rates become acceptable when the laser transition energy is in the region of five to seven times the highest phonon energy; thus we may expect laser action to become difficult at wavelengths greater than about one half of the infrared transparency limit - a rule supported by many laser ion/host systems, but with occasional exceptions.

Thus in order to seek new solid state hosts we require very low phonon energies (for a five micron laser below about  $300\text{cm}^{-1}$ ) or equivalently infrared transmission to beyond ten microns at least. Additionally of course we must be able to dope the solid with a suitable ion. Low phonon energies suggests chalcogenides, but no suitable crystals are available; an interesting candidate would be  $\text{La}_2\text{S}_3$ , but its high melting point and corrosive properties make crystal growth a daunting task. An alternative route is the heavy halides, obvious choices being for example  $\text{LaCl}_3$  and  $\text{LaBr}_3$ . These materials are extremely hygroscopic and thus difficult to cut, polish, coat and maintain in good condition. Additionally although the melting points are quite low they are corrosive and easily contaminated with oxyhalides which ruin the crystals. Thus the solid state route would entail a substantial, costly material development program. A further limitation is that such hosts are really only suited to  $3+$  ionisation state lanthanide ions with a limited range of ion size, so the choice of dopant is limited. If a different dopant type or concentration is required, a co-dopant is to be used etc a new, costly crystal must be grown and laser rods fabricated incurring long delays.

## 1.2 Solvents for liquid phase lasers

The use of the liquid phase eliminates many of these problems, but is only well established for dye lasers. The high frequency of the H-O, C-H and C=O vibrations limits infrared transparency and makes organic solvents or water useless for infrared operation. In the past a considerable amount of work was done on  $\text{POCl}_3$  and  $\text{SeOCl}_2$  solvents which eliminate these vibrations, but with the advent of good solid hosts (silicate and phosphate glasses, YAG,

YLF) the work was dropped. These solvents are corrosive, fume, have high thermal expansion and Raman cross sections, and offer no advantage over a good solid state host.

A new solvent should offer the following properties to be a good laser host:-

- transparency at pump and laser wavelengths
- low vibrational and rotational Raman cross section
- chemically inert
- low non radiative relaxation rates
- dissolve species of interest
- low toxicity, non corrosive.

### 1.3 Properties of liquid Xenon.

Xenon is a unique material. It has a critical temperature of 289.7K (16.3C) and a critical pressure of 5.84MPa (58.4 bar) so both liquid and supercritical phases are readily accessible; for example at -1.8C the vapour pressure of liquid Xe is 4MPa (40 bar). Maintenance of the liquid phase requires modest cooling (<16.3C) but the pressure presents no serious engineering or safety hazard. Liquid cored fibres can easily withstand this pressure, making small, sealed off systems a possibility. We address the other properties in turn.

Transparency. Obviously there are no rotational or vibrational transitions. Xenon is transparent from the far infrared to deep into the ultraviolet. No other solvent has such a wide transparency range. Weak 'pressure induced' transitions may occur in the far infrared.

Raman cross section. There are no rotational or vibrational states so no such cross sections exist. Since the first electronic state is deep in the ultraviolet electronic Raman scattering is not a concern for visible or infrared applications.

Inertness. Whilst a few xenon fluorides and oxyfluorides do exist, for all practical purposes xenon is totally inert. The extreme inertness of xenon may be exploitable to avoid solvent related photochemical effects in UV dye lasers.

Relaxation rates. Again since there are no rotational or vibrational states many non radiative relaxation routes are blocked. The large mass of the xenon atom reduces the efficiency of relaxation via translational energy, owing to the requirement to conserve momentum. In fact xenon is unique in that dissolved HF shows clear resolved rotational structure in the liquid phase in this solvent! Vibrational relaxation of hydrogen halides in liquid xenon is known to be exceptionally slow, with a probability as low as  $3 \cdot 10^{-8}$  for HCl in liquid Xe.

Solvent action. Liquid and supercritical xenon are surprisingly good solvents. They are used by chemists to perform chromatography, and a range of organic, organo metallic, hydrogen halides and halogens are known to dissolve. Purely ionic materials are not expected to dissolve. In practice the ability to predict solubility appears to be poor, and direct measurements are needed. For many laser applications very low solubility (to  $< 100\text{ppm}$ ) would be adequate, especially in the liquid cored fibre geometry.

Toxicity etc. The material is obviously non toxic and non corrosive. Although we experienced very severe engineering difficulties ultimately the modest cooling ( $< 16.3\text{C}$  for liquid) and pressures are little more than inconvenient. The material is relatively expensive ( $\sim 14\text{US}$  per litre atmosphere which yields several cc of solvent depending on the conditions) but not excessively so; the price is very variable, depending on current availability as a by product of oxygen production.

## **2 Safety**

### **2.1 General Comments**

It was apparent that safety would be a major consideration in the design and operation of the experimental apparatus. Safety requirements had considerable cost and timescale implications. Some of the hazards are somewhat unconventional in nature, and are combined in rather unusual ways. This section sets out our approach to these issues.

### **2.2 Metal Components**

All valves and fittings were of high-grade stainless steel construction, rated by the manufacturer for pressures considerably in excess of those to be used in the experiment, or indeed pressure in the cylinders supplying it. At first sight therefore no hazard should arise in normal circumstances.

However since Xenon is to be condensed in sample cylinders and in the sample cell, if the liquid sample is isolated and allowed to warm up extreme over-pressure could be generated. This situation could relatively easily arise through operator error. For this reason pressure relief valves are located in several places to minimise the possibility of failure by this mechanism; they were set to 1000 PSI.



The cell is intended to operate at temperatures down to  $\sim -20^{\circ}\text{C}$ , whilst the sample cylinders used to generate the pressure are cooled to 77°K to condense the Xenon. Concern arose over the possibility of brittle failure of components at low temperature. For the cell we were advised that stainless steel and can head screws of standard type would be above their ductile to brittle transition temperature and hence acceptable. *For the small cylinders there was more concern, because of the immersion in liquid nitrogen; however the Xenon will of course follow its vapour pressure curve, so that at 77K the pressure is negligible, rising as the cell warms.* We were unable to obtain a definite statement from the manufacturers as to the ductile-to-brittle transition temperature of the cylinders, but their verbal advice, and a comparison of the likely values for comparable steels with the Xenon vapour pressure curve, indicated that no problem was likely. However since brittle failure of these cylinders would be a very hazardous event, almost certainly causing injury, additional precautions were taken by placing a plastic fragment shield in front to the apparatus when cooling the cylinders.

In designing the sample cell the only significant concern regarding stress is the bolts securing the window flanges. A safety factor of four was included in all calculations. There was also concern that excessive tightening of the bolts could cause failure when pressure was applied. The problem is that on tightening the bolt *much of its tensile strength can be 'used up'* by the bolting force before pressure is applied. Hence the bolts were only tightened just sufficiently to bring the associated flange to a metal-to-metal contact.

During pressure testing, long sections of appropriately rated metal tubing had to be used to connect to the pressure source; they were firmly screwed down at regular intervals to prevent dangerous 'whipping' in the event of a (very unlikely) fitting failure.

### 2.3 Windows

Window failure was viewed from the outset as a relatively likely occurrence. The windows were designed, as is normal practice, using a safety factor of four. However since the materials are intrinsically brittle this (widely used and accepted!) approach is of dubious validity; relatively minor scratches, impacts or 'stress raisers' can cause a brittle component to fail even with a safety factor four when a ductile component would easily survive.

By far the most common components designed in this way are vacuum windows; the relatively low differential pressure, absolutely limited to one atmosphere, combined with the fact that fragments resulting from window failure go in, usually away from the operator, make them relatively trouble free.

In contrast for a pressure window we have much larger differentials, (i.e. higher stored energy densities) no limit on the differential (to ~60 atmospheres in normal use, 120 atmospheres on test in this application) and fragments will be ejected by a 'gas gun' effect, potentially at the operator. The issue of window failure is therefore the most serious safety hazard in the experiment.

Our view therefore was that the window cannot, under any circumstances, be regarded as entirely safe. Operator safety must be guaranteed by appropriate protection and procedures. Window failure is to be viewed, at all times, as a probable event! This is especially the case of course during testing under nitrogen over pressure.

With this in mind the following precautions were taken.

- during pressure testing the sample cell was contained in a small wooden, open-topped box of heavy construction and no visual observations made of the windows.
- when the cell is pressurised high-impact full-face shields are worn at all times by all personnel in the laboratory, and laboratory coats worn (no 'shirt sleeves' personnel).
- the cell windows were never observed directly at a range of less than one metre.
- closer observation was made rarely, after careful consideration, and by using a 45° mirror plus an additional large sheet of 0.25" perspex in the viewing path.

No window failure occurred in which fragments were violently ejected, but several BaF<sub>2</sub> windows did fail, and in our view these precautions were amply justified!

## 2.4 Chemical Hazard

The nitrogen test gas and Xenon solvent only present a possible asphyxiation hazard, and the volumes present are too small for this to be significant.

For a considerable number of the materials to be dissolved in the Xenon relatively little is known about the toxic hazard. During loading of the cell little problem arises, routine precautions being adequate to protect the operator from exposure (gloves, segregation etc.) In the event of catastrophic window failure the Xenon solvent will 'flash off' leaving the (very small quantity) of solute presumably very finely dispersed in the air. Standing instructions were to evacuate the laboratory for at least an hour and ventilate it thoroughly if this happened, but no such event in fact occurred, all windows failed during nitrogen testing, not in use.

### **3 Design of the Filling System**

#### **3.1 General Considerations**

In designing the filling system the overriding consideration is safety. Aside from the obvious use of high quality parts with appropriate ratings, this dictates that each independently isolatable part of the system must be protected by separate relief valves. The second major consideration is that Xenon is normally supplied at relatively low pressures, typically 800 PSI or less. We require to fill the cell to pressures up to, or slightly exceeding the critical pressure of 58.22 atmospheres or 855.8 PSI; hence the cylinder as delivered is incapable of filling the cell! Whilst it might be possible to fill at lower temperature where the required pressure is reduced (say at  $-20^{\circ}\text{C}$ , 393 PSI) and then warm the cell to operating temperature, the large thermal mass of the cell would make this a slow, inconvenient operation, and the chance of leakage etc. during temperature cycling much increased. Furthermore at best only about half the contents of the Xenon cylinder could be used. Hence some method is needed to raise the Xenon pressure before filling the cell. Small volume, non-contaminating high pressure booster pumps would be an ideal, simple solution, but no suitable pump was located after an extensive search. A design was therefore evolved in which the Xenon pressure was increased by successive condensation of the gas in an accumulation cylinder, see **figure 1**.

#### **3.2 Principle of the Design**

The method of operation is described by reference to the numbered valves and gauges in **figure 1**. The apparatus is divided into three sections, each having its own gauges and relief valves and being isolatable from the other sections by shut-off valves.

Operation of the system is as follows. Initially all the valves except the high pressure cylinder valve are open, and the system is evacuated to an indicated pressure of  $\sim < 0.01$  Torr. Evacuation to much lower pressure is effectively prevented by the poor vacuum conductance of the small-bore, high pressure piping. For this reason three vacuum access points are provided via V2, V4 and V7, close to the three items of significant volume, the accumulation cylinders and the cell.

Because lower pressure evacuation was not feasible, valves V2, V4 and V7 are then shut, the system filled to approximately atmospheric pressure with Xenon from the supply cylinder, and is then re-evaluated via the same three valves. This procedure will reduce any contamination from atmospheric air to levels  $\sim < 10\text{ppm}$ . On first evacuating the system it was left pumping for some hours and warmed with a hot air blower to eliminate any traces of moisture.

After evacuation the entire system is re-filled to the maximum currently available cylinder pressure (assuming this to be lower than the required pressure. If this is not the case, for example with a nearly new cylinder, the following steps are not needed).

Valves V5 and V1 are now closed, and cylinder two cooled in liquid nitrogen, thereby condensing all the gas in sections one and two into cylinder two. As soon as G1 and G2 show that the gas has condensed, V3 is closed isolating section one, V1 opened and cylinder one is re-filled with Xenon to the desired pressure. V1 is re-closed, V3 re-opened, and the Xenon transfers into cylinder two, monitored by the fall in gauge one and transient rise in gauge two.

By noting the pressure of each fill of cylinder one, and from a knowledge of the (approximately equal) volumes of sections one and two, the total amount of Xenon accumulated as solid in cylinder two is known.

In calculating the amounts of gas to be used in filling cylinder one it is essential to recognise that Xenon is a severely non-ideal gas when in the vicinity of its critical temperature - as is frequently the case during these operations! Since the critical temperature is  $16.3^\circ\text{C}$ , and we are deliberately filling the cell to near critical conditions, this non ideal behaviour is **NOT** a

minor correction but a major effect.

A particular hazard arises at this point since if cylinder two is allowed to warm up with V3 and V5 still closed very high pressures can be generated if the room temperature is significantly above the critical temperature (16.6°C) or if in a cold room below critical temperature the cylinders were to be severely over-filled and become full of liquid. Gauge two monitors this situation, and relief valve two protects against it.

Once sufficient Xenon has been accumulated in cylinder two it can be transferred to the cell. Prior to this valve three is closed after the last transfer, and to reduce the risk of air in leakage cylinder one is re-filled to one atmosphere.

To effect the transfer valve five could simply be opened and cylinder two then allowed to warm up. This however causes an abrupt fall in the cell pressure as its gas freezes out of the cell into cylinder two, followed by a rise as the cylinder warms. The forces on the cell window thus abruptly reverse direction, as the cell pressure is initially at or above atmospheric, falls well below, then rises to operating pressure. This procedure initiated a window leak on one occasion. The preferred method is therefore to observe the rising pressure on gauge two as cylinder two warms up, and open valve five when the pressure indicated on gauge two is equal to, or slightly greater than that on gauge three. Clearly it is important not to allow the gauge two pressure to greatly exceed that of gauge three or there will be an abrupt pressure jump which could initiate window fracture. In practice in normal laboratory temperatures the rise of pressure through the appropriate region occurs slowly and there is no difficulty in opening valve five at the appropriate time.

Two other items should be noted. The fine metal frit filter above the cell prevents any solid materials loaded into the cell being transferred into the line and causing leaks by lodging under valve seats etc. The non-return valve in section three is optional. Its use enforces 'dumping' of the Xenon after each experiment, which is relatively costly, but prevents any Xenon with dissolved materials being transferred into the pressure accumulation system and thereby contaminating it.

In practice due to other difficulties we were unable to conduct enough experiments in which the xenon could in principle have been recovered for xenon usage to become a serious issue, so that the non-return valve was used to avoid contamination.

Although some initial difficulties were experienced obtaining a satisfactory leak-tight system (partly due to a faulty-as-supplied tank adapter fitting connecting to the cell having excessive O-ring groove depth) the filling system ultimately worked as designed. At typical operating pressures of 70-60 bar no pressure changes beyond those ascribable to room temperature changes or gauge drift could be observed over periods in excess of 24 hours, showing the system to be adequately leak tight.

## **4 Cell Design**

### **4.1 Requirements**

The cell had to satisfy the following requirements

- operate safely from  $-20^{\circ}\text{C}$  to  $+30^{\circ}\text{C}$  at pressures up to 60 bar
- minimum volume
- sufficient aperture for easy use in spectrophotometers
- small enough to fit in spectrophotometer sample cell compartments
- windows to remain condensation free
- provide maximum possible transmission range, as a minimum covering the visible plus as far as practical into the infrared
- provide a geometry suitable for fluorescence measurements
- be corrosion/contamination resistant
- provide good temperature uniformity (as solubility versus temperature curves are unknown, no precise tolerance can be set;  $\sim 1^{\circ}\text{C}$  was taken as a target).

In our initial proposal construction of two cells, one with two inline windows and a ten centimetre path length, and one short path four windowed cell for fluorescence work was envisaged (to economise on xenon usage). During detailed design it became clear that it was difficult to construct a short path fluorescence style cell with low volume owing to strength and bolting requirements, and the two cells were combined into a single three windowed unit, the fourth window in the fluorescence geometry not being essential.

## 4.2 Body Design

These are a challenging set of requirements to meet simultaneously. It was decided at the outset that for safety and to minimise problems of welds, corrosion etc. the main cell should be of single-piece, "machined-from-solid", stainless steel construction. Previous experience showed that attempts to avoid condensation by external dry gas shielding at these temperatures are frequently unsuccessful unless in a fully enclosed, controlled environment such as a glove box. It was thus deemed essential to have double windows with a vacuum interspace to avoid the outer surface falling to low temperatures; infrared spectroscopy is of course particularly sensitive to condensed water or ice layers, and such layers could confuse the spectra obtained, window layers being indistinguishable from Xenon contamination. The overall cell design is shown in **figure 2**, window views in **figure 3**, and solute load arrangements in **figure 4**.

Previous experience also suggested that leakage across O-rings can be a serious problem if they become hardened by exposure to low temperatures. Given the large pressure differential in this apparatus considerable care was taken over the exact choice of O-ring material by taking advice from the manufacturers, utilising materials with good chemical inertness which remain soft at low temperature (excluding, for example, the well known 'viton' which is too hard when cold).

## 4.3 Window Choice

Experiments were expected to be conducted in the visible (laser dyes and excitation of fluorescence from infrared emitting species) and infrared (absorption spectroscopy to confirm solute dissolution, etc.) Visible transparency was also highly desirable for (cautious!) direct observation of liquid levels and solute behaviour. For these reasons windows transparent to visible light were considered vital. This ruled out choices such as germanium, gallium arsenic, silicon and cadmium telluride, with good strength and infrared transparency but no visible transmission. Zinc selenide transmits into the red, which was deemed insufficient, and is also of very high cost, and so was ruled out. Any oxide based glass, including silica, only transmit to  $\sim 3000\text{cm}^{-1}$  which does not cover the main infrared diagnostic region. The choice is thus restricted to alkali and alkaline earth halides (eg. KCl, KBr,  $\text{CaF}_2$ ,  $\text{BaF}_2$ ) and sapphire which are commercially available as infrared windows. Of these the alkali halides are very weak with a modulus of rupture as low as 400 PSI, they are also hygroscopic and soft. The

choice thus reduces to  $\text{CaF}_2$ ,  $\text{BaF}_2$  or sapphire, all of which are transparent in the visible but vary in their infrared cut-off.

Of these  $\text{BaF}_2$  has the best infrared transmission, extending to  $\sim 800\text{cm}^{-1}$  in these fairly thick windows and providing good infrared diagnostics.  $\text{CaF}_2$  is significantly worse, limited to  $\sim 1100\text{cm}^{-1}$ , whilst sapphire cuts off near  $1700\text{cm}^{-1}$ .

Of the three  $\text{BaF}_2$  is weakest with a modulus of rupture of  $\sim 3900$  PSI,  $\text{CaF}_2$  somewhat better at 5300 PSI and sapphire much the highest at  $\sim 70,000$  PSI. The halides cleave along the 111 direction, sapphire does not cleave, and all three materials have stable surfaces in air.

Calculations showed that for  $\text{BaF}_2$  a thickness to diameter ratio of 0.48 would be needed to achieve a safety factor of four at 60 bar. Given the small unsupported apertures required of at most 10-15mm for the inner, pressure window  $\text{BaF}_2$  was chosen as the window material initially. A further factor was the ready availability of  $\text{BaF}_2$  from a local supplier who had previously proved being reliable at much lower cost than sapphire; the deciding factor however was the better infrared transmission of  $\text{BaF}_2$ .

#### 4.4 Temperature control

The ability to vary the temperature over the range from  $-20^\circ\text{C}$  to  $+30^\circ\text{C}$  is needed. This was provided by drilling interconnecting holes through the cell body block and plugging unwanted drill entrance holes in such a way as to provide a continuous cooling channel through which antifreeze was pumped. The cooled, temperature controlled antifreeze was supplied from a commercial, compressor driven cooler. This arranged proved highly satisfactory.

#### 5 System Testing

The cell was tested in a heavy construction wooden box using nitrogen. Initial testing of both the cell and filling apparatus was done under vacuum with a standard leak detector. The filling system was pre-tested at pressure and, once some minor leaks were eliminated, zero pressure decay achieved.



The cell was fitted with  $\text{BaF}_2$  window and the pressure steadily raised, initially to ~60 bar only (operating pressure) prior to a 120 bar test. It immediately became apparent that a leak had developed when the system was sealed off, as pressure decay was severe; there was no explosive pressure loss or audible failure.

On de-pressurising the cell the  $\text{BaF}_2$  windows were found to be full of internal cleavage planes visible as bright reflecting surfaces, although they remained physically intact as solid discs.

Initially it was thought possible that some error had occurred in cell tolerances, window thickness etc. causing the window edge to be 'nipped' and cleavage initiated. The spare window set was installed with extreme care after extensive dimensional checking and the cell re-tested. No pressure decay occurred initially, but by 15 bar the window had again cleaved!

The reasons for this failure was discussed at length with the suppliers and other experts, but it has not been clearly resolved. All the  $\text{BaF}_2$  windows tried failed in a similar manner. The issue may be one of the material or polishing (cost considerations prevented trying several suppliers) or, possibly more probably, is caused by detailed stress patterns around the window edge supports.

## 6 Window Modifications

It ultimately became clear that within the timescale and budget available the barium fluoride window problem could not be resolved. The only viable choice within these and technical restraints was sapphire (zinc selenide would be highly desirable as an alternate.) The cell was designed for thick barium fluoride windows, and sapphire windows of the same thickness were of excessive cost, so thin windows were used (they easily withstand the pressure owing to the increase in modulus of rupture by a factor of over ten.) This entailed the introduction of double sided, o-ring sealed spacers into the interspace between the windows. With careful attention to tolerances on window and spacer thickness, o-ring compression etc installation of the sapphire windows proved successful and a leak tight, pressure proof cell was finally obtained.

A major disadvantage of the change to sapphire windows is the loss of infrared transmission below about  $1700\text{cm}^{-1}$ . Much of the valuable low energy information is lost, severely restricting the utility of infrared spectroscopic diagnostics. This proved a serious problem.

## 7 Experiments and Results

Unfortunately the heavy consumption of staff and technician time and need for window replacements etc very severely restricted the experimental work, despite the use of considerable resources from within the group.

Initially a blank infrared spectrum was run of the nitrogen purged cell. The featureless spectrum shows the cut off of the sapphire windows at  $1700\text{cm}^{-1}$ , the overall transmission below  $2500\text{cm}^{-1}$  of  $\sim 40\%$  being as expected for the four sapphire windows in the path (two 'double glazed' windows) (74%) and some aperturing of the beam by the cell. The significant thickness of sapphire also slightly defocusses the instrument and contributes to the loss. These results were entirely satisfactory.

For each experiment the cell was dismantled, thoroughly cleaned, reassembled, pressure tested to ensure leak tight performance, evacuated whilst warm to remove any residual volatile contamination, and the solute then loaded via the bottom entry provided for this purpose whilst nitrogen purged. Finally the cell was evacuated twice with an intervening xenon flush, and filled with liquid xenon at 10C. Initially this procedure was followed without any solute; the results are shown in figure 5.

A serious problem immediately became apparent. The very strong absorption band in the  $2850\text{-}3000\text{cm}^{-1}$  region is obviously the C-H stretch vibration of a hydrocarbon - but only xenon was deliberately present. The weaker bands between  $3500$  and  $4500\text{cm}^{-1}$  appear to be traces of water plus hydrocarbon overtone and combination bands.

It was thought initially that some residual contamination might have been transferred to the cell from the filling system, despite the precautions taken to avoid this. However repeated refilling did not change the strength of these bands and it was concluded that they are from residual hydrocarbon and water contamination in the xenon.

It was immediately obvious that this contamination ruled out any laser schemes relying on low non radiative relaxation rates. The major point of the xenon solvent system is the absence of high vibrational frequency solvent molecule modes; the presence of O-H and C-H contamination vitiates this advantage.

These bands, plus the cut off imposed by the sapphire windows, unfortunately essentially render the use of infrared diagnostics to check solute solubility in the xenon impossible.

In a final attempt to obtain some results attempts were made to dissolve some laser dyes which would provide strong fluorescence 'signatures' in the UV/visible region. Rhodamine 6G, rhodamine B and p-terphenyl were tried. In the first two cases there was no visible evidence of dissolution, and no evidence of fluorescence in the xenon when excited with a 100mW 5145A argon laser. For p-terphenyl there was tentative evidence of some dissolution visually from the appearance of the solute (the solution would be colourless) but no fluorescence could be detected under excitation from a UV filtered xenon arc lamp. We do not regard this result as definitive, as being principally an infrared laboratory we are not well equipped for this experiment; as noted above our infrared diagnostics were rendered useless by the enforced use of sapphire windows and the hydrocarbon impurity in the xenon.

#### **8 Comments and possible future work**

We are very conscious that the experiments we were able to run were very limited. The combined impact of the window failures and hydrocarbon impurity problem was devastating to this very limited scale program. Unfortunately solving these difficulties fully required resources in excess of those available without further external funding.

We now have a working filling system and cell. The original ideas on which the program is based remain valid, but effectively unexplored. In order to continue the cell should be provided with alternative ZnSe windows to re-enable infrared diagnostics; previous experience suggests that strength should not be a serious issue with ZnSe. Secondly the hydrocarbon needs removing. The most likely candidate is methane, and this could be eliminated by repeated freeze-pump-thaw cycles in situ in the filling cylinders. Water vapour should be removed by installing a cooled molecular sieve trap into the xenon filling line prior to the cell. With these difficulties overcome, the prospects remain good that some highly novel laser systems could be found.

#### **9 Staff**

Staff employed on this project were Dr Elaine Blackwood (Research Assistant) and Professor Harvey N Rutt. Various Departmental technical staff were employed, in particular Mr R Webb for extensive mechanical construction work. No degrees were awarded as a result of this work.

## 10 Publications and inventions

No publications or patented inventions arose from the work, although we still believe this to be a possible result of any further program. No specific 'coupling activities' arose from the work. No visits were made to, or received from Air Force or other DoD laboratories.

## 11 References and Bibliography

E. Aprile, R. Mukherjee et al.

Measurements of the lifetime of conduction electrons in liquid xenon

Nuclear Instruments and Methods in Physics Research, A300 pp 343-350 1991

M. A. Bernikov, M. O. Bulanin et al.

Evolution of IR spectra of HF in xenon on the gas-liquid transition

Opt. Spectrosc. (USSR), Vol 69, pp 712-713 1990

C. L. Brooks III, S. A. Adelman.

Dynamics of liquid state chemical reactions: Photolysis of molecular iodine in liquid xenon

J. Chem. Phys., Vol 80, pp 5598-5609 1984

M. O. Bulanin, I.M. Grigorev et al.

Evidence of gas-like rotation of molecules in absorption spectra of HF in liquid Xe

Opt. Spectrosc. (USSR), Vol 68, pp 566-567 1990

J. Chesnoy

Vibrational energy relaxation of hydrogen chloride in liquid and solid xenon solutions

J. Chem. Phys., Vol 83, pp 2214-2223 1985

J. Chesnoy

Vibrational Spectroscopy of Hydrogen Chloride in Liquid and Solid Xenon Solutions

Chemical Physics Letters, Vol 114, pp 220-228 1985

George Davidson and Claire L. Davies

Raman spectroscopy in liquid xenon solutions: Trifluorohalomethanes

Spectrochimica Acta, Vol 45A, pp 371-373 1989

M. A. Healy, T. J. Fenkins et al.

Infrared detection in supercritical fluid chromatography using xenon

Trends in Analytical Chemistry, Vol 10, pp 92-97 1991

Erich Knozinger, Walter Schuller et al.

Structure and Dynamics in Pure and Doped Rare-gas Matrices

Faraday Discuss. Chem. Soc., Vol 86, pp 285-293 1988

J. Thomas Knudtson

Vibrational Relaxation of HCl in HCl/Liquid Xenon Mixtures

Chemical Physics Letters, Vol 104, pp 71-78 1984

J. Thomas Knudtson, Yannis P. Vlahoyannis et al.

Relaxation of HCl in liquid xenon solution by vibration-vibration energy transfer

J. Chem. Phys., Vol 82, pp 4381-4382 1985

J. Thomas Knudtson, Eric Weitz

Infrared spectra and band strengths of the fundamental and first overtone of HCl and DCl in liquid xenon solutions

J. Chem. Phys., Vol 83, pp 927-933 1985

Val J. Krukonis, Mark A. McHugh et al

Xenon as a Supercritical Solvent

J. Phys. Chem., Vol 88, pp 2687-2689 1984

J. Perez, S. Velasco et al.

Infrared Spectra of HCl, HBr and HI Dissolved in Liquid Xenon

J Molec Liquids, Vol 45, pp 71-76 1990

J. Perez, D. Luis et al.

Infrared spectra of diatomic polar molecules in rare-gas liquids. 1. Spectral theory  
J. Chem. Phys., Vol 91, pp 3435-3442 1989

J. Perez, D. Luis et al.

Infrared spectra of diatomic polar molecules in rare-gas liquids. 2. Application to the HCl in  
Ar, Kr, and Xe solutions  
J. Chem. Phys., Vol 91, pp 3443-3449 1989

P. M. Rentzepis, D. C. Douglass

Xenon as a solvent  
Nature, Vol 293, pp 165-166 1981

M. Seidl, J. Kaa et al.

Relaxation of singlet molecular oxygen in the liquid and gas phase up to 154 K  
Chemical Physics, Vol 157, pp 279-285 1991

R. D. Smith, S. L. Frye et al.

Solvent Properties of Supercritical Xe and SF<sub>6</sub>  
J. Phys. Chem., Vol 91, pp 3059-3062 1987

K. G. Tokhadze, M. A. Bernikov et al.

Investigation of the νHF absorption band contour in a complex of HF with ether in the  
gaseous phase and in solution in liquid Xe  
Opt. Spectrosc. (USSR), Vol 65, pp 322-326 1988

James J. Turner, Martyn Poliakoff et al.

Infrared Spectroscopy and Chemistry in Liquid Rare-gas Solvents  
Faraday Discuss. Chem. Soc., Vol 86, pp 271-284 1988

Yannis P. Vlahoyannis, Herman Krueger et al

Vibration-Vibration energy transfer processes in liquid xenon: A measurement of the rate constant for

Chemical Physics Letters, Vol 121, pp 272-278 1985

Yannis P. Vlahoyannis, Herman Krueger et al.

V-V energy transfer in the HCl-CO system: A comparison between measurements in the gas phase and in the liquid xenon solution

J. Chem. Phys., Vol 86, pp 3311-3317 1987

Lawrence Wiedeman, Mario E. Fajardo et al.

Electronic Relaxation of  $\text{Xe}_2^+\text{Cl}^-$  in solid and liquid xenon

J. Phys. Chem., Vol 92, pp 342-246 1988

Xiaobing Xu, Soo-Chang Yu et al.

Ultrafast transient Raman investigation of geminate recombination and vibrational energy relaxation in iodine: The role of energy relaxation pathways to solvent vibrations

J. Chem. Phys., Vol 95, pp 2445-2457 1991

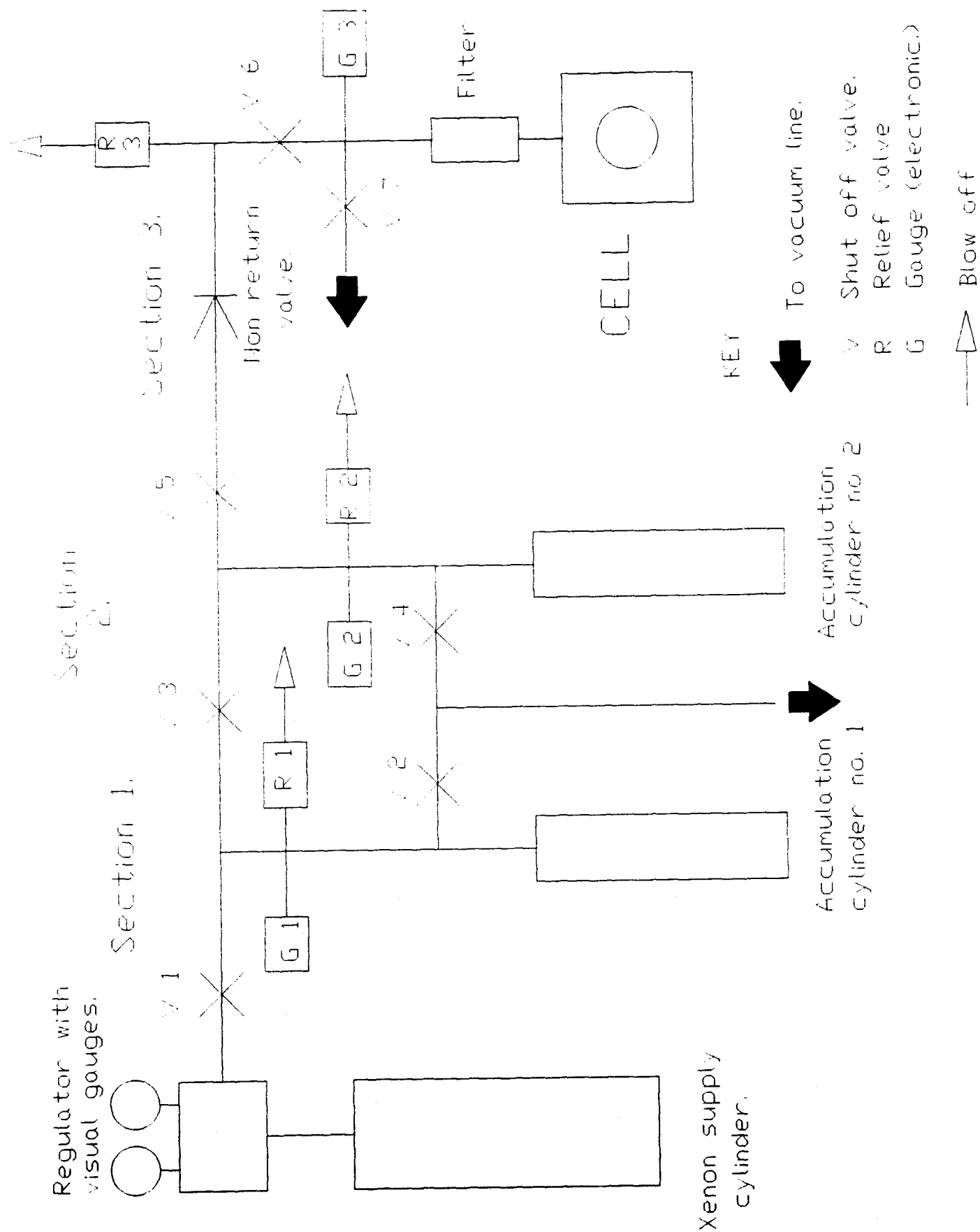


Figure 1

Xenon Filling System



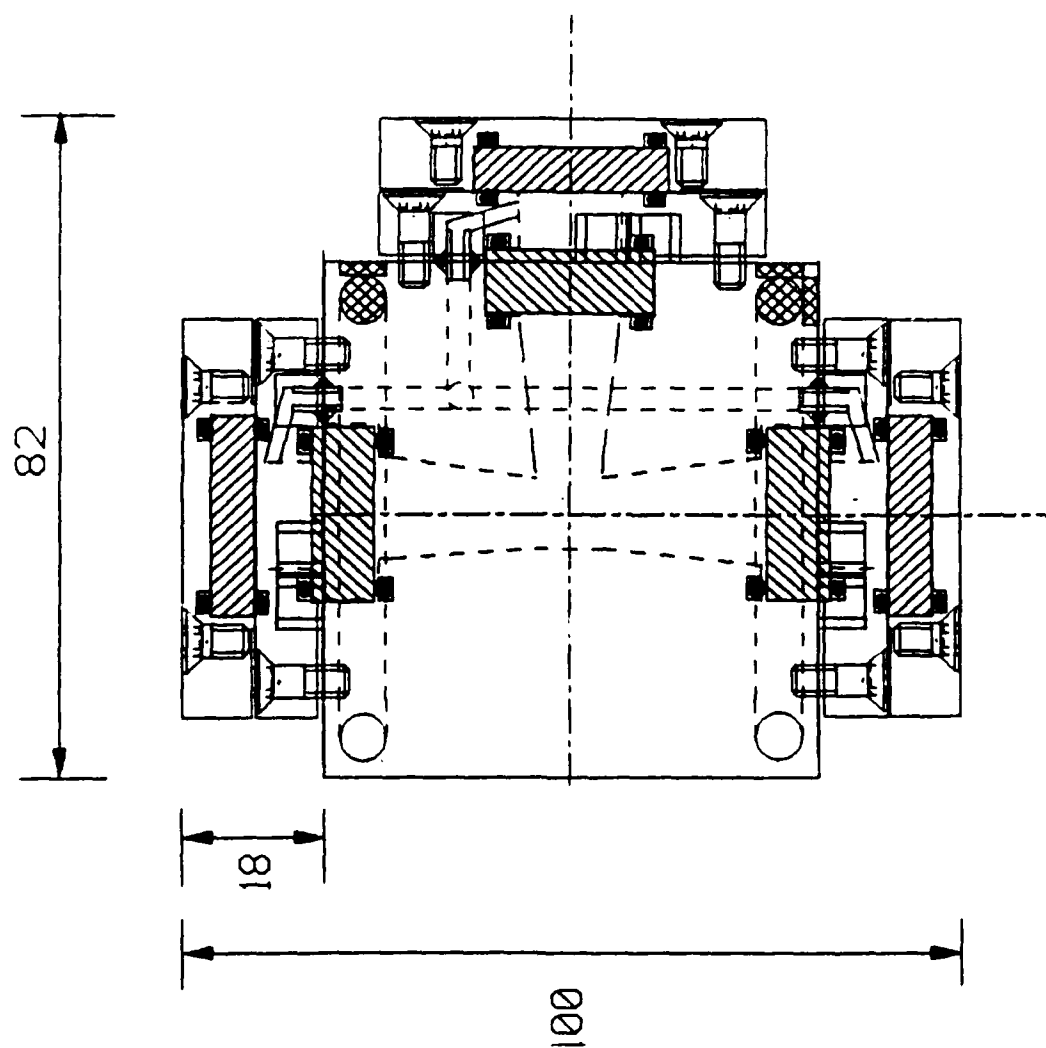


Figure 2

Cell assembly, top view excluding gas fill port for clarity

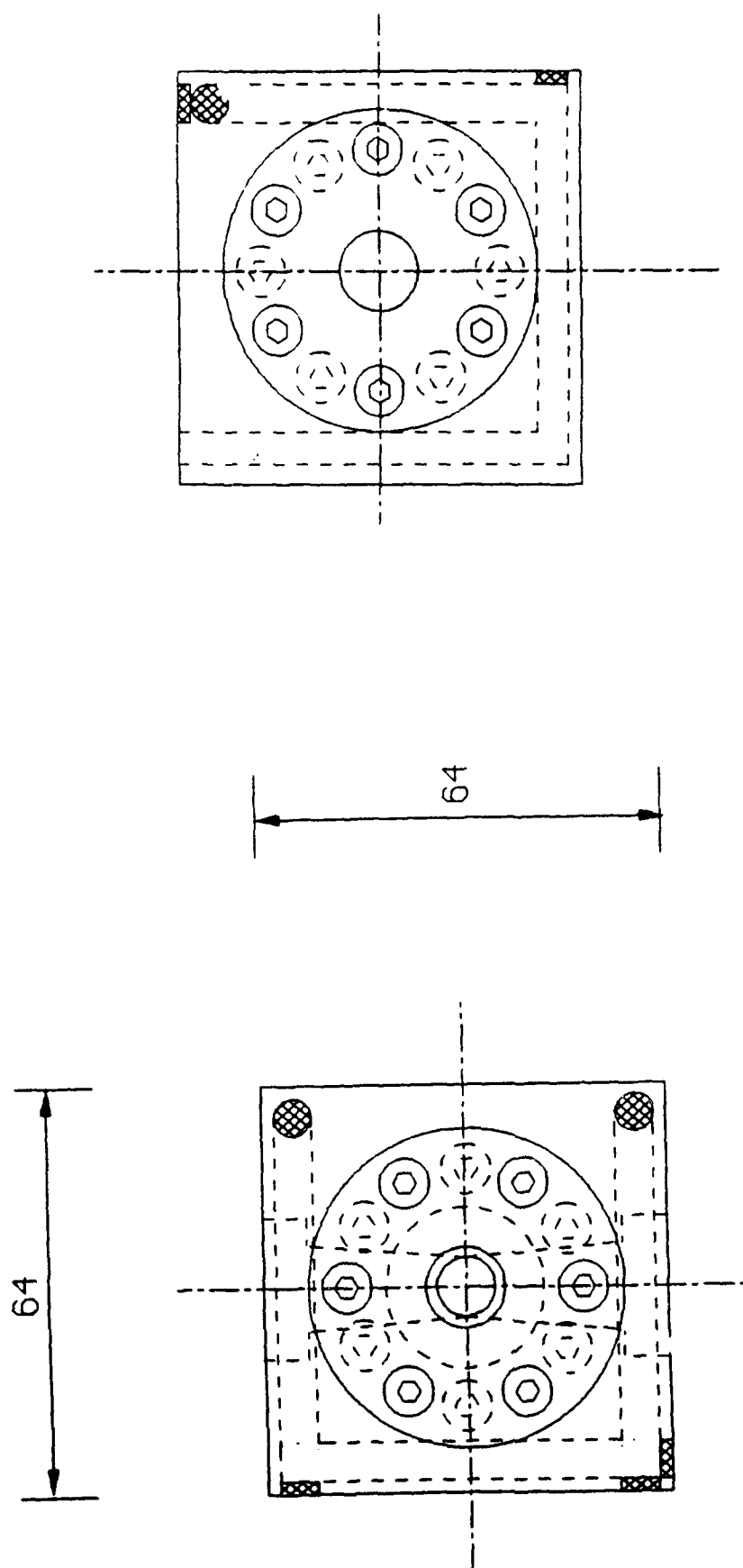


Figure 3 Cell, view on window flanges showing cooling channels

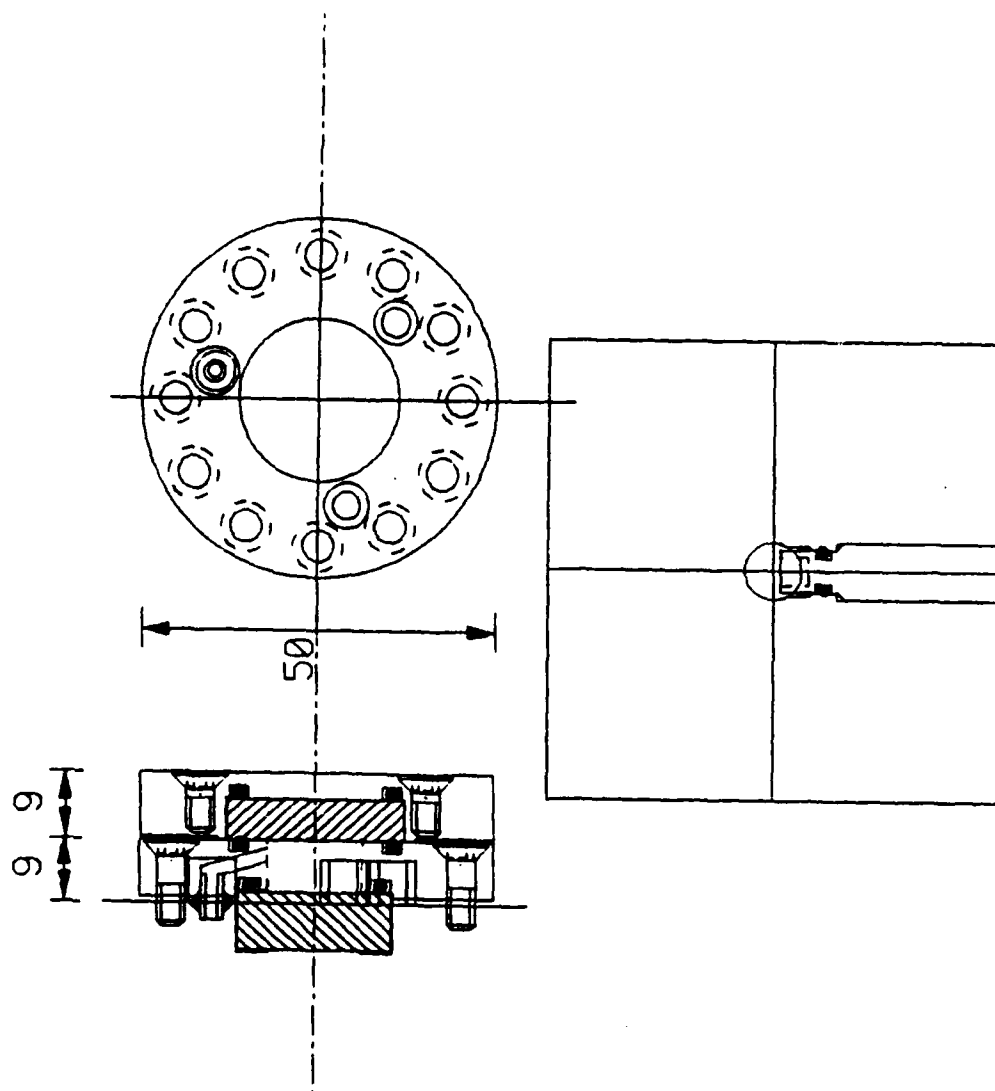


Figure 4

Cell, part views of double window and solute load arrangement

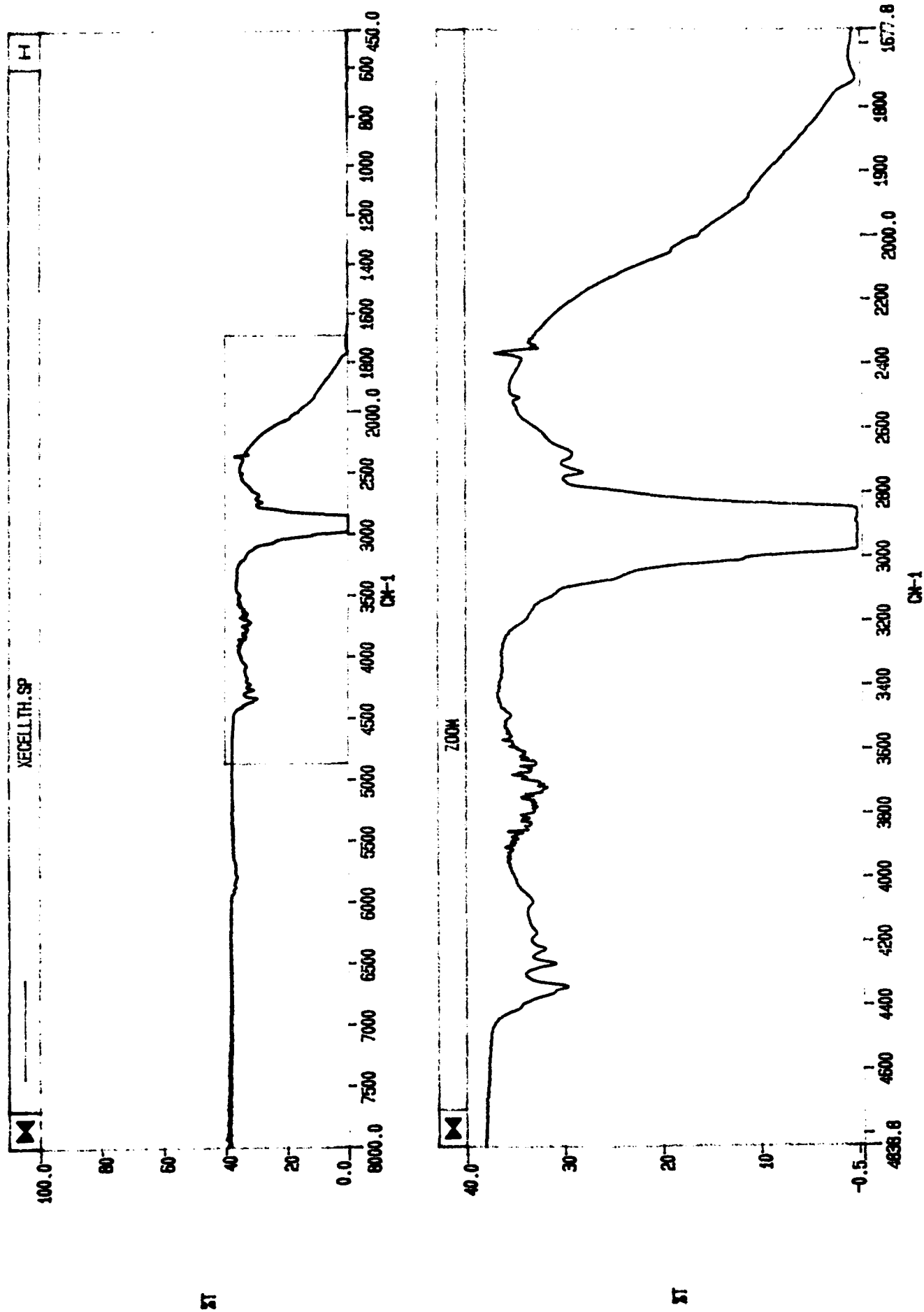


Figure 5 Infrared spectrum of liquid xenon fill, 10C